Patent Claims:

1. Organic semiconductors comprising
   (A) at least one polymer,
   (B) at least one structural unit L=X, where the following applies to the symbols used:

L is on each occurrence, identically or differently, $(R^1)(R^2)C$, $(R^1)P$, $(R^1)As$, $(R^1)Sb$, $(R^1)Bi$, $(R^1)(R^2)(R^3)P$, $(R^1)(R^2)(R^3)As$, $(R^1)(R^2)(R^3)Sb$, $(R^1)(R^2)(R^3)Bi$, $(R^1)(R^2)S$, $(R^1)(R^2)Se$, $(R^1)(R^2)Te$, $(R^1)(R^2)S(=O)$, $(R^1)(R^2)Se(=O)$ or $(R^1)(R^2)Te(=O)$;

X is on each occurrence, identically or differently, O, S, Se or $N\text{-}R^4$, with the proviso that X is not S or Se if L stands for S, Se or Te;

R^1, R^2, R^3 is on each occurrence, identically or differently, H, F, CN, $N(R^4)_2$, a straight-chain, branched or cyclic alkyl, alkoxy or thioalkoxy group having 1 to 40 C atoms, which may be substituted by R^5 or may also be unsubstituted, where one or more non-adjacent CH_2 groups may be replaced by $-R^6C=CR^6-$, $-C\equiv C-$, $Si(R^6)_2$, $Ge(R^6)_2$, $Sn(R^6)_2$, C=O, C=S, C=Se, $C=NR^6$, -O-, -S-, $-NR^6-$ or $-CONR^6-$ and where one or more H atoms may be replaced by F, Cl, Br, I, CN or NO_2, or an aromatic or heteroaromatic ring system having 1 to 40 C atoms, which may be substituted by one or more radicals R^5, where two or more substituents R^1, R^2 and/or R^3 may also with one another form a mono- or polycyclic, aliphatic or aromatic ring system; all substituents R^1 to R^3 on one structural unit here must not be H or F; the groups R^1 to R^3 may furthermore optionally have bonds to the polymer;

R^4 is on each occurrence, identically or differently, a straight-chain, branched or cyclic alkyl or alkoxy chain having 1 to 22 C atoms, in which, in addition, one or more non-adjacent C atoms may be replaced by $-R^6C=CR^6$, $-C\equiv C-$, $Si(R^6)_2$, $Ge(R^6)_2$, $Sn(R^6)_2$, $-NR^6-$, -O-, -S-, -CO-O-, -O-CO-O-, where, in addition, one or more H atoms may

be replaced by fluorine, an aryl, heteroaryl or aryloxy group having 1 to 40 C atoms, which may also be substituted by one or more radicals R^6, or OH or $N(R^5)_2$;

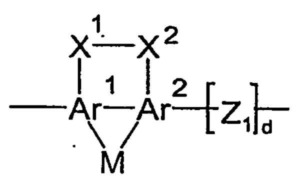
R^5 is on each occurrence, identically or differently, R^4 or CN, $B(R^6)_2$ or $Si(R^6)_3$,

R^6 is on each occurrence, identically or differently, H or an aliphatic or aromatic hydrocarbon radical having 1 to 20 C atoms;

and

(C) at least one triplet emitter;

with the proviso that mixtures of two polymers in which the first polymer contains covalently bonded triplet emitters and the other is a copolymer comprising TPD units and diphenyl sulfone ether or diphenyl ketone ether units are excluded; and furthermore with the proviso that polymers containing on the one hand covalently bonded triplet emitters and on the other hand units of the formula (a) are excluded from the invention:



formula (a)

in which Ar^1 and Ar^2 each independently denote a tetravalent aromatic hydrocarbon group or a tetravalent heterocyclic group;

one of the units X^1 and X^2 denotes C(=O) or $C(R^1)(R^2)$ and the other denotes O, S, C(=O), S(=O), SO_2, $Si(R^3)(R^4)$, $N(R^5)$, $B(R^6)$, $P(R^7)$ or $P(=O)(R^8)$; where the radicals R^1, R^2, R^3, R^4, R^5, R^6, R^7 and R^8 in the formula (a) each independently denote a hydrogen atom, a halogen atom, an alkyl group, an alkoxy group, an alkylthio group, an alkylamino group, an aryl group, an aryloxy group, an arylthio group, an arylamino group, an arylalkyl group, an arylalkoxy group, an arylalkylthio group, an arylalkylamino group, an acyl group, an acyloxy group, an amide group, an imine group, a substituted silyl group, a substituted silyloxy group, a substituted silylthio group, a substituted silylamino group, a monovalent heterocyclic group, an arylalkenyl group, an arylethynyl group or a cyano group,

M denotes a group which is represented by formula (b), formula (c) or formula (d)

$-Y^1-Y^2-$ formula (b)

in which Y^1 and Y^2 each independently denote O, S, C(=O), S(=O), SO_2, $C(R^9)(R^{10})$, $Si(R^{11})(R^{12})$, $N(R^{13})$, $B(R^{14})$, $P(R^{15})$ or $P(=O)(R^{16})$, where the radicals R^9, R^{10}, R^{11}, R^{12}, R^{13}, R^{14}, R^{15} and R^{16} in the formula (b) each independently denote a hydrogen atom, a halogen atom, an alkyl group, an alkoxy group, an alkylthio group, an alkylamino group, an aryl group, an aryloxy group, an arylthio group, an arylamino group, an arylalkyl group, an arylalkoxy group, an arylalkylthio group, an arylalkylamino group, an acyl group, an acyloxy group, an amide group, an imine group, a substituted silyl group, a substituted silyloxy group, a substituted silylthio group, a substituted silylamino group, a monovalent heterocyclic group, an arylalkenyl group, an arylethynyl group or a cyano group,

where Y^1 and Y^2 are not identical if Y^1 is not $C(R^9)(R^{10})$ or $Si(R^{11})(R^{12})$.]

$-Y^3=Y^4-$ formula (c)

in which Y^3 and Y^4 each independently denote N, B, P, $C(R^{17})$ or $Si(R^{18})$;

the radicals R^{17} and R^{18} in the formula (c) each independently denote a hydrogen atom, a halogen atom, an alkyl group, an alkoxy group, an alkylthio group, an alkylamino group, an aryl group, an aryloxy group, an arylthio group, an arylamino group, an arylalkyl group, an arylalkoxy group, an arylalkylthio group, an arylalkylamino group, an acyl group, an acyloxy group, an amide group, an imine group, a substituted silyl group, a substituted silyloxy group, a substituted silylthio group, a substituted silylamino group, a monovalent heterocyclic group, an arylalkenyl group, an arylethynyl group or a cyano group;

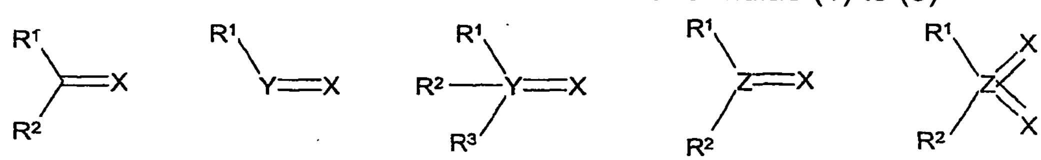
$-Y^5-$ formula (d)

in which Y^5 denotes O, S, C(=O), S(=O), SO_2, $C(R^{19})(R^{20})$, $Si(R^{21})(R^{22})$, $N(R^{23})$, $B(R^{24})$, $P(R^{25})$ or P(=O)(R);

where the radicals R^{19}, R^{20}, R^{21}, R^{22}, R^{23}, R^{24}, R^{25} and R^{26} in the formula (d) each independently denote a hydrogen atom, a halogen atom, an alkyl group, an alkoxy group, an alkylthio group, an alkyl-

amino group, an aryl group, an aryloxy group, an arylthio group, an arylamino group, an arylalkyl group, an arylalkoxy group, an arylalkylthio group, an arylalkylamino group, an acyl group, an acyloxy group, an amide group, an imine group, a substituted silyl group, a substituted silyloxy group, a substituted silylthio group, a substituted silylamino group, a monovalent heterocyclic group, an arylalkenyl group, an arylethynyl group or a cyano group;
Z_1 denotes $-CR^{36}=CR^{37}-$ or $-C \equiv C-$; R^{36} and R^{37} each independently denote a hydrogen atom, an alkyl group, an aryl group, a monovalent heterocyclic group or a cyano group; d denotes 0 or 1.

2. Organic semiconductors according to Claim 1, characterised in that the structural units L=X are selected from the formulae (1) to (5)



formula (1) formula (2) formula (3) formula (4) formula (5)

where the symbols used have the following meaning:

X is on each occurrence, identically or differently, O, S, Se or $N-R^4$, with the proviso that X cannot be S or Se for formulae (4) and (5);

Y is on each occurrence, identically or differently, P, As, Sb or Bi;

Z is on each occurrence, identically or differently, S, Se or Te;

R^1 to R^6 have the same meaning as described under Claim 1.

3. Organic semiconductors according to Claim 1 and/or Claim 2, characterised in that they comprise at least 0.5% by weight of at least one polymer, at least 1% by weight of at least one structural unit L=X or a structural unit of the formulae (1) to (5) and at least 0.1% by weight of at least one triplet emitter.

4. Mixtures (BLEND1) according to one or more of Claims 1 to 3, comprising

(A) 5 – 99.9% by weight of at least one polymer (POLY1) which comprises 1 – 100 mol% of one or more recurring units

(MONO1) containing at least one structural unit L=X or at least one structural unit of the formula (1) to (5),

and

(B) 0.1 – 95% by weight of one or more triplet emitters (TRIP1).

5. Mixtures (BLEND2) according to one or more of Claims 1 to 3, comprising

(A) 0.5 – 99% by weight of at least one polymer (POLY2) which comprises 0.5 – 99.5 mol% of one or more triplet emitters (TRIP2) covalently bonded,

and

(B) 1 – 99.5% by weight of at least one compound (COMP1) which contains at least one structural unit L=X or at least one structural unit of the formula (1) to (5) and is capable of forming glass-like layers at room temperature.

6. Mixtures (BLEND3) according to one or more of Claims 1 to 3, comprising

(A) 0.5 – 98.9% by weight of any desired polymer (POLY3),

and

(B) 1 – 99% by weight of at least one compound (COMP1) which contains at least one structural unit L=X or at least one structural unit of the formula (1) to (5) and is capable of forming glass-like layers at room temperature,

and

(C) 0.1 – 95% by weight of one or more triplet emitters (TRIP1).

7. Mixtures (BLEND4) according to one or more of Claims 1 to 3, comprising

(A) 0.5 – 99% by weight of at least one polymer of any desired type (POLY3);

and

(B) 1 – 99.5% by weight of a compound (TRIP3) which contains at least one structural unit L=X or at least one structural unit of the formula (1) to (5) covalently bonded to one or more triplet emitters, where the bonding between the triplet emitter and the

structural unit L=X can take place in any desired positions of the two units, with the restriction that at least one group X in (TRIP3) must be in free form and not coordinated to a metal atom.

8. Polymers POLY4 comprising
   (A) 1 – 99.9 mol% of one or more recurring units MONO1 containing at least one structural unit L=X, where symbols L, X, R^1, R^2, R^3, R^4, R^5 and R^6 have the same meaning as described under Claim 1;
   (B) 0.1 – 95 mol% of one or more triplet emitters TRIP2.

9. Organic semiconductors according to one or more of Claims 1 to 8, characterised in that the polymers (POLY1 to POLY4) are conjugated, partially conjugated, cross-conjugated or non-conjugated.

10. Organic semiconductors according to one or more of Claims 1 to 9, characterised in that the polymers POLY1 to POLY4 contain further structural elements.

11. Organic semiconductors according to one or more of Claims 1 to 10, characterised in that the following applies to the symbols of the formulae (1) to (5):
    X stands for O, S or N-R^4;
    Y stands for P or As;
    Z stands for S or Se;
    R^1 – R^6 are defined according to Claim 1 and 2, where at least one of the substituents R^1 to R^3 on each structural unit of the formula (1) to (5) represents an aromatic or heteroaromatic ring system having 1 to 40 C atoms, which may be substituted by one or more substituents R^4 or unsubstituted.

12. Organic semiconductors according to Claim 11, characterised in that the following applies to the symbols of the formulae (1) to (5):
    X stands for O or N-R^4;
    Y stands for P;

Z stands for S;

$R^1 - R^6$ are defined according to Claim 1 and 2, where all substituents R^1 to R^3 on each structural unit of the formula (1) to (5) represent an aromatic or heteroaromatic ring system having 1 to 40 C atoms, which may be substituted by one or more substituents R^4 or unsubstituted.

13. Organic semiconductors according to one or more of Claims 1 to 12, characterised in that at least one of the radicals R^1 to R^3 contains a 9,9'-spirobifluorene.

14. Organic semiconductors according to one or more of Claims 1 to 13, characterised in that the recurring units (MONO1) which contain structural elements L=X or structural elements of the formula (1) to (5) are selected from the formulae (6) to (148), which may be substituted or unsubstituted.

15. Organic semiconductors according to one or more of Claims 1 to 14, characterised in that the polymers are selected from the classes of the aromatic polyketones, aromatic polyphosphine oxides or aromatic polysulfones, each of which may also be substituted for better solubility, the polycarboxylic acid derivatives, main-chain polyesters, side-chain polyesters, poly(glycolic acids), poly(lactic acids), poly(ε-caprolactones), polyacrylates, poly(hydroxybenzoic acids), poly(alkylene terephthalates), polycarboxylic anhydrides, polyamides, poly(ε-caprolactams), polypeptides, polyaramids, polybenzamides, polyimides, poly(amide-imides), poly(ester-imides), poly(ether-imides), polycarbonates, poly(ester-co-carbonates), poly(isocyanurates), polyurethanes, polyester-polyurethanes, poly(terephthalates), poly(acrylates), poly(phenyl acrylates), poly(cyanoacrylates), poly(vinyl esters), poly(vinyl acetates), side-chain polyphosphine oxides, polyether ketones (PEK), polyether sulfones, polysulfonamides, polysulfonimides, poly(vinyl ketones), aromatic polyvinyl ketones, substituted or unsubstituted poly(vinylbenzophenones), polystyrene-analogous ketones, polycarbazenes, polynitriles, polyisonitriles, polystyrene, PVK (polyvinylcarbazole) or derivatives thereof.

16. Organic semiconductors according to one or more of Claims 1 to 13, characterised in that the compound (COMP1) which contains structural elements L=X or structural elements of the formulae (1) to (5) is selected from the formulae (6) to (148), which may be substituted or unsubstituted.

17. Organic semiconductors according to one or more of Claims 1 to 13, characterised in that the compound (TRIP3) contains structural elements which are selected from the formulae (6) to (148), which may be substituted or unsubstituted.

18. Organic semiconductors according to one or more of Claims 1 to 17, characterised in that the triplet emitters contain atoms from the Periodic Table of the Elements having an atomic number of greater than 36.

19. Organic semiconductors according to Claim 18, characterised in that the triplet emitters contain d or f transition metals.

20. Organic semiconductors according to Claim 19, characterised in that the triplet emitters contain metals from group 8 to 10.

21. Organic semiconductors according to one or more of Claims 1 to 20, characterised in that further molecules, which may be of low molecular weight, oligomeric, dendritic or polymeric, are admixed with the organic semiconductors.

22. Organic semiconductors according to Claim 21, characterised in that compounds containing structural units L=X or structural units of the formula (1) to (5) may additionally be admixed with the mixture.

23. Organic semiconductors according to one or more of Claims 1 to 22, characterised in that the total proportion of structural units of the formula (1) to (5) is 10 – 50 mol%.

24. Polymers containing one or more structural units of the formula (1) to (5) and 9,9'-spirobifluorene units.

25. Use of an organic semiconductor according to one or more of Claims 1 to 23 in organic light-emitting diodes (PLEDs), organic solar cells (O-SCs), organic laser diodes (O-lasers) or in non-linear optics.

26. Electronic component which comprises one or more active layers, where at least one of these active layers comprises one or more organic semiconductors according to one or more of Claims 1 to 23.

27. Electronic component according to Claim 26, characterised in that it is an organic light-emitting diode, an organic solar cell or an organic laser diode.